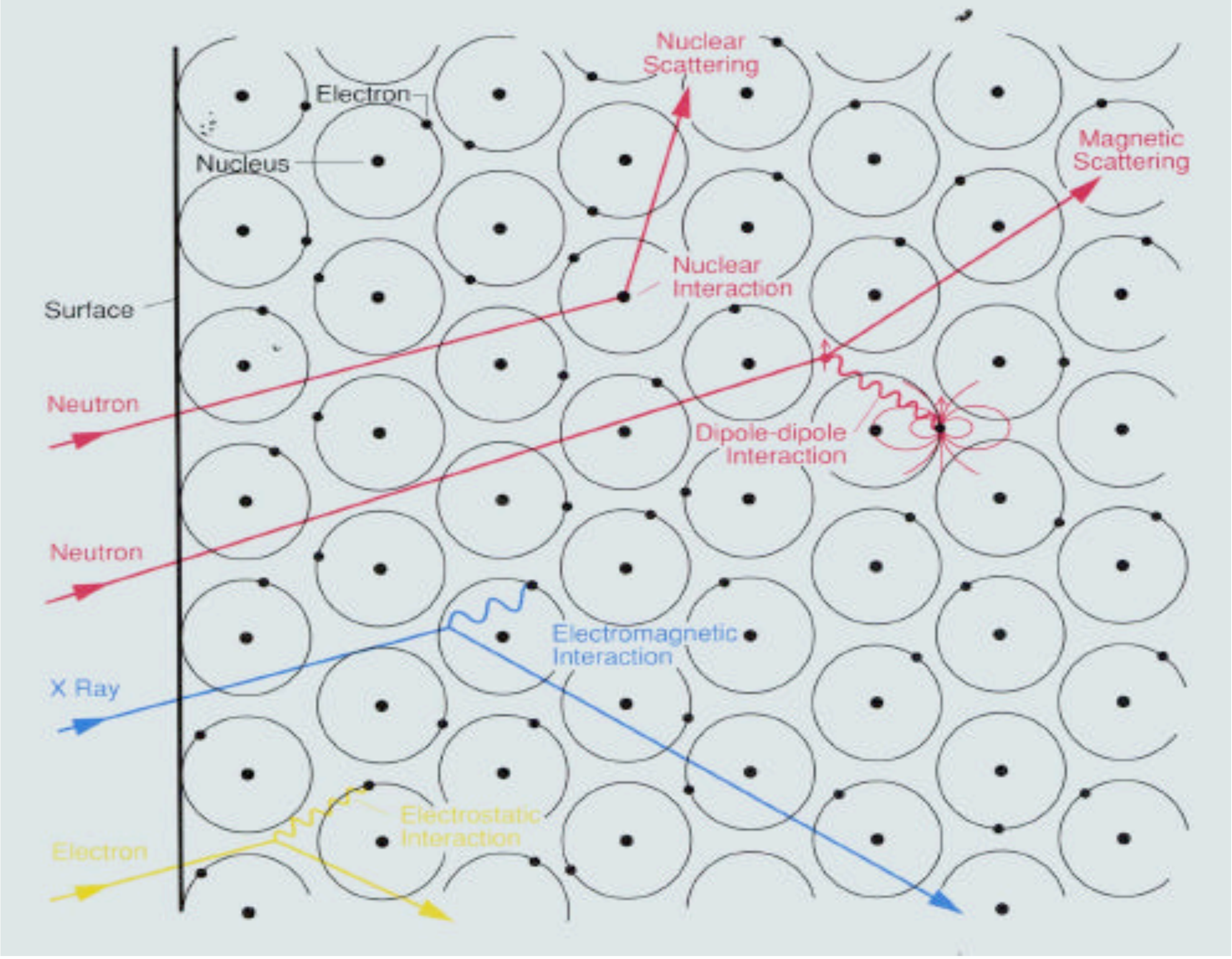
Neutron diffraction

Rob McQueeney

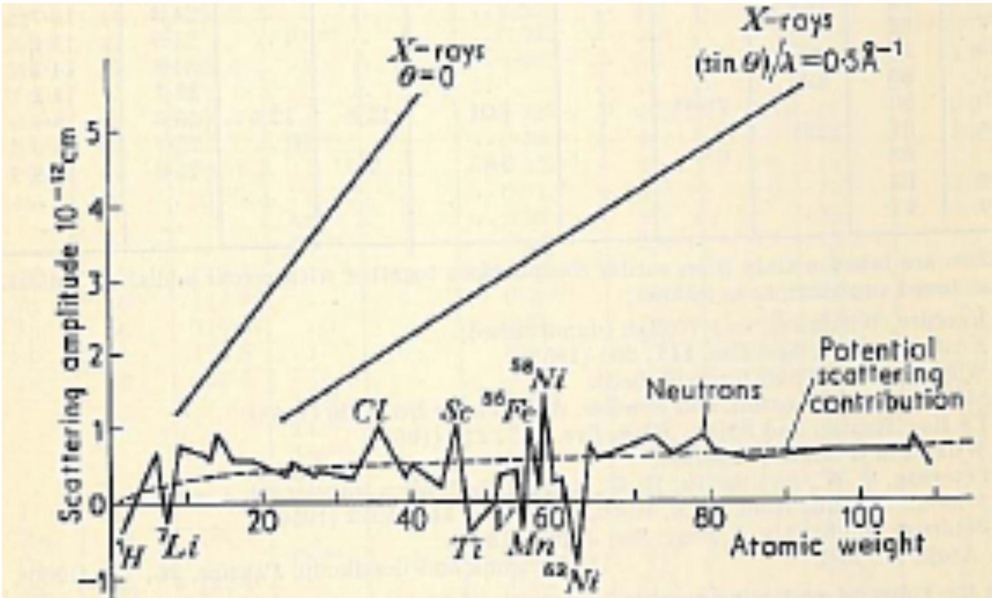
Different probes



Different probes

	NEUTRONS	X-RAYS	ELECTRONS
Wavelength range	0.4 - 10 Å	0.1 - 5 Å	0 .04 - 0.2 Å
Energy range	0.001 - 0.5 eV	3000 - 100000 eV	6000 - 120000 eV
Cross-section	10^{-25} barns	10^{-25} Z^2 barns	~10^{-22} barns
Penetration depth	~ cm	~ μm	~ nm
Typical flux	10^{11} s^{-1} m^{-2}	10^{24} s^{-1} m^{-2}	10^{26} s^{-1} m^{-2}
Beam size	mm-cm	μm-mm	nm-μm
Typical sample	Any bulk sample	Small crystals, powders, surfaces	Surfaces, thin films, grains, gases
Techniques	**Diffraction** Inelastic scattering Reflectivity	Diffraction Photon absorption Photoemission Inelastic scattering	Microscopy Diffraction Emission spectroscopy EELS
Phenomena	**Magnetic/crystal structures** collective excitations (phonons, spin waves) electronic excitations (crystal-field, spin-orbit)	Crystal structures, electronic transitions (photoemission, absorption),	microstructure crystal structures electronic transitions

Neutron cross-section

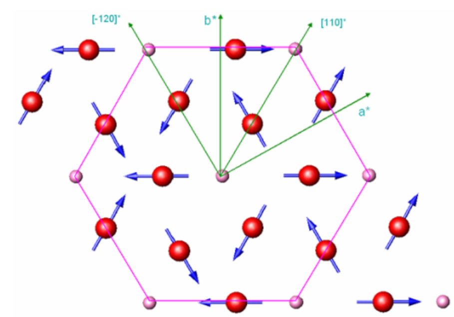


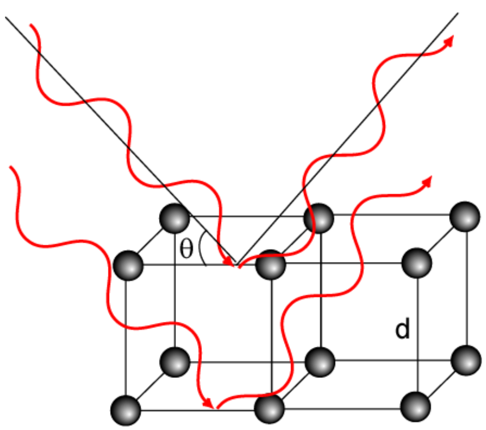
- **Nuclear property**
  - Random with Z
  - Depends on isotope
  - Depends on nuclear spin
  - Absorption can be problem

	Abundance (%)	Cross-section (bn)	Absorption (bn)
Gd	---	180	49700
152Gd	0.2	13	735
154Gd	2.1	13	85
155Gd	14.8	66	61100
156Gd	20.6	5	1.5
157Gd	15.7	1044	259000
158Gd	24.8	10	2.2
160Gd	21.8	10.52	0.77

Why neutrons??

- Penetration ~ centimeters, bulk probe
- Sensitivity to low-Z
- Isotopic contrast
- Wavelength range ~ interatomic spacing (1-2 Å) → diffraction
  - interacts with nuclei
  - Interacts with magnetic moment of unpaired e^-
- Can measure crystal and magnetic structures





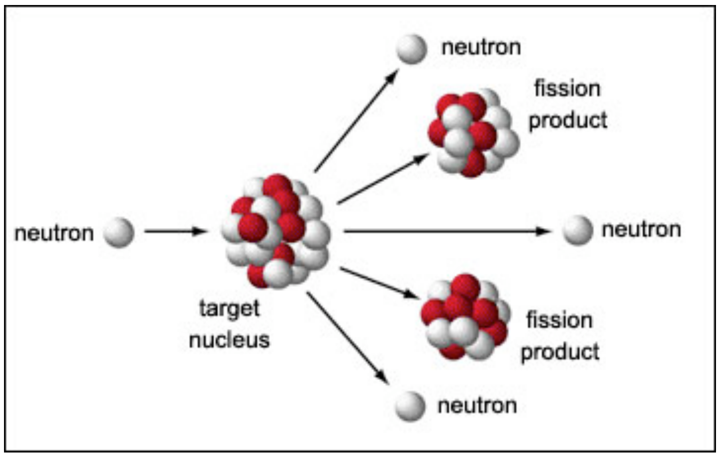
Elastic scattering - Bragg's Law

$2d\sin\theta = n\lambda$

Producing neutrons

Fission

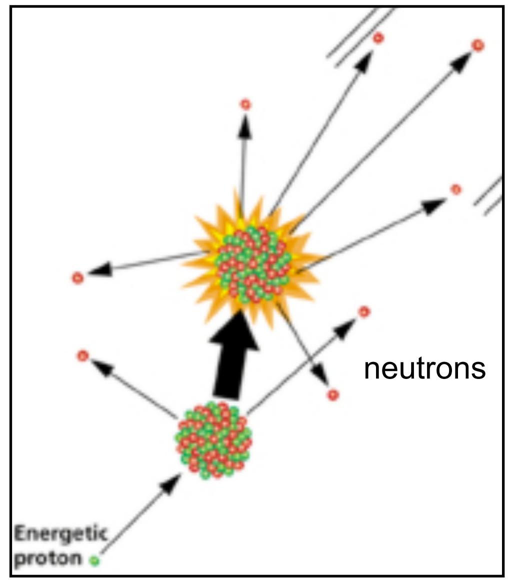
Nuclear reactor



Moderators →Cold-Thermal

Spallation

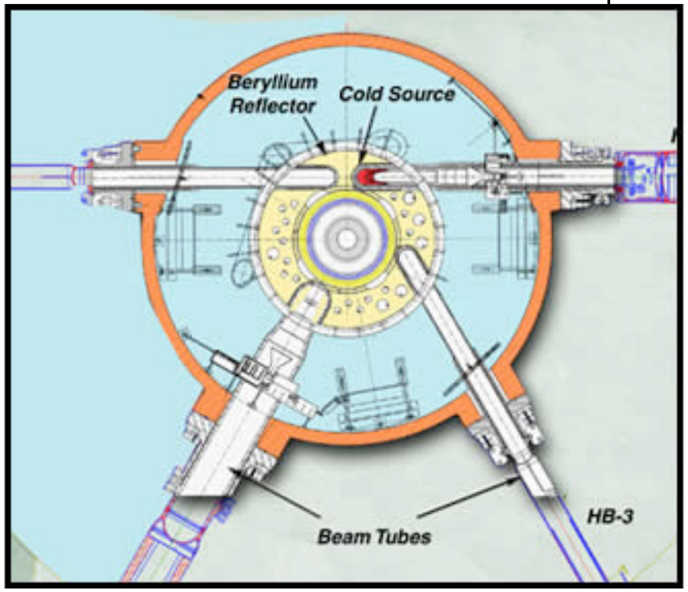
Particle accelerator

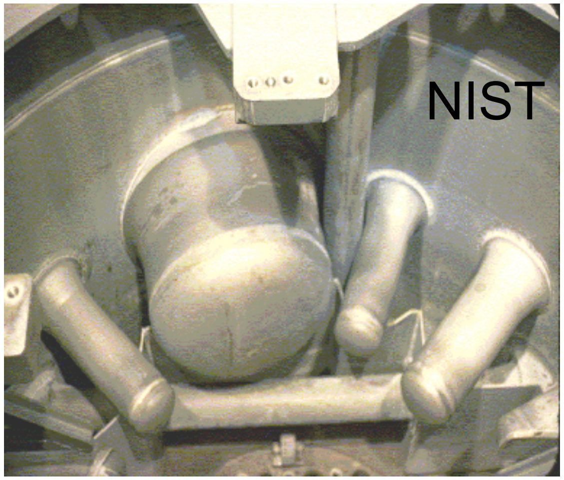


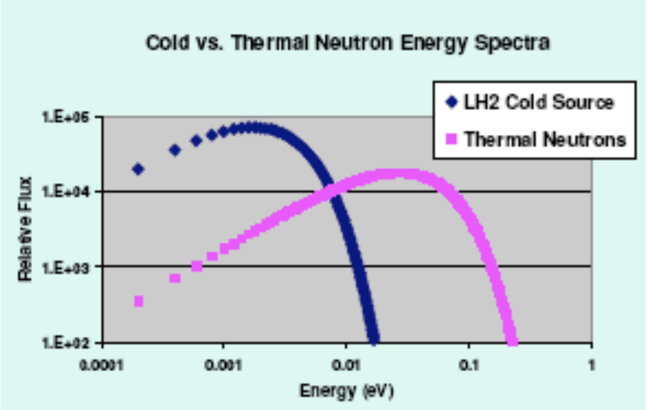
Moderators →Cold-Epithermal

Neutrons by reactor fission

High flux isotope reactor - ORNL







Length scales

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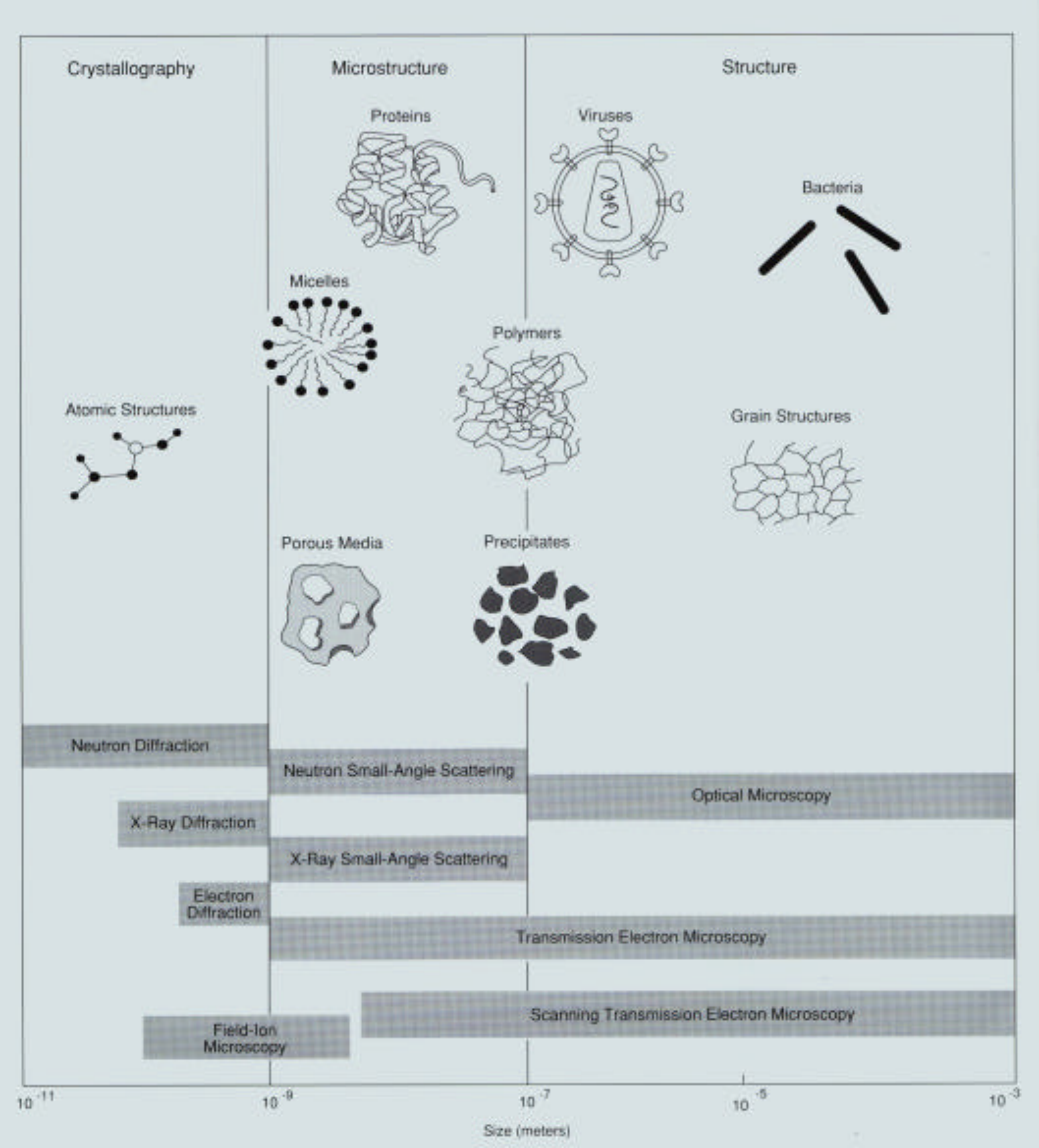
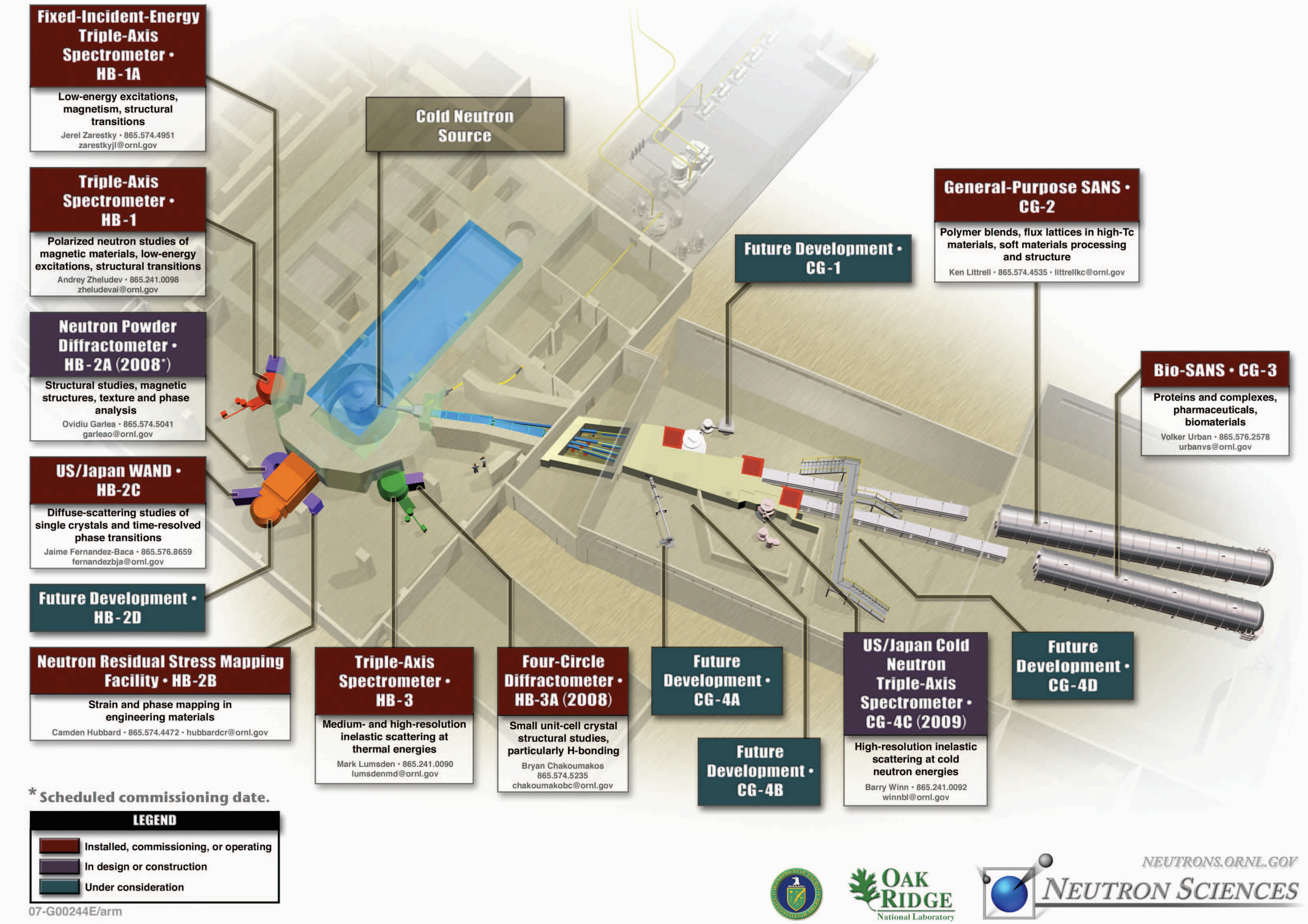


High Flux Isotope Reactor at Oak Ridge National Laboratory

The United States' highest flux reactor-based source of neutrons for condensed matter research

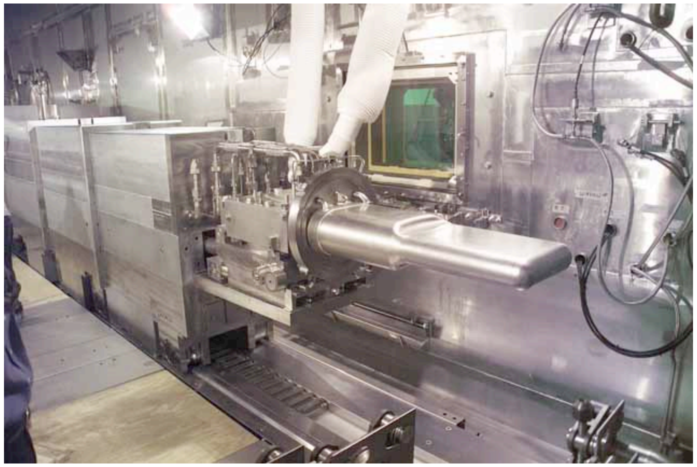
ORY



Neutrons by pulsed spallation

Spallation Neutron Source (ORNL)

Target-moderator system



SNS liquid Hg target

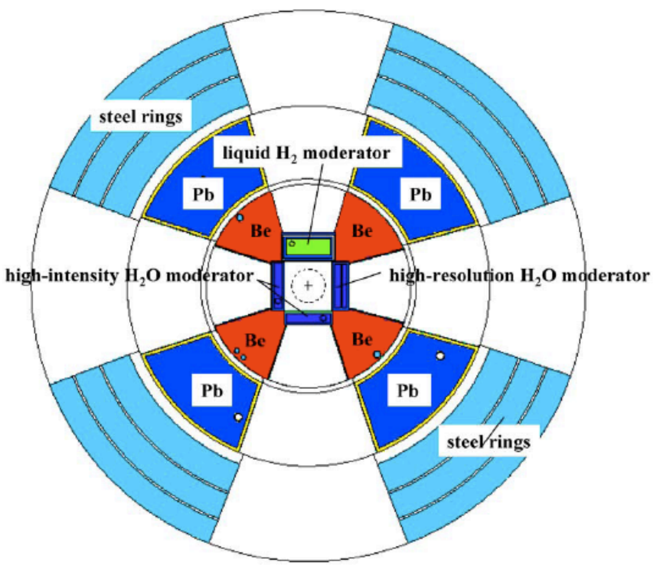
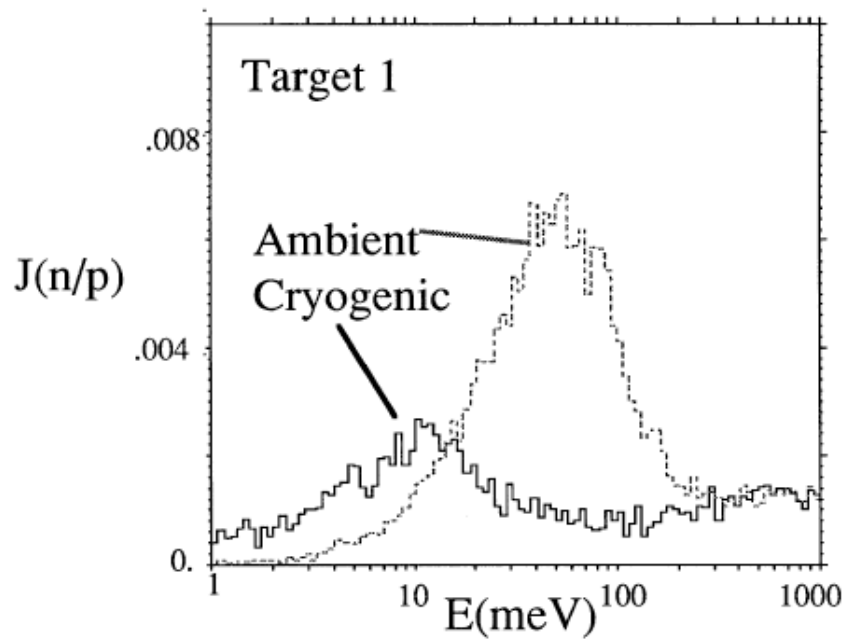
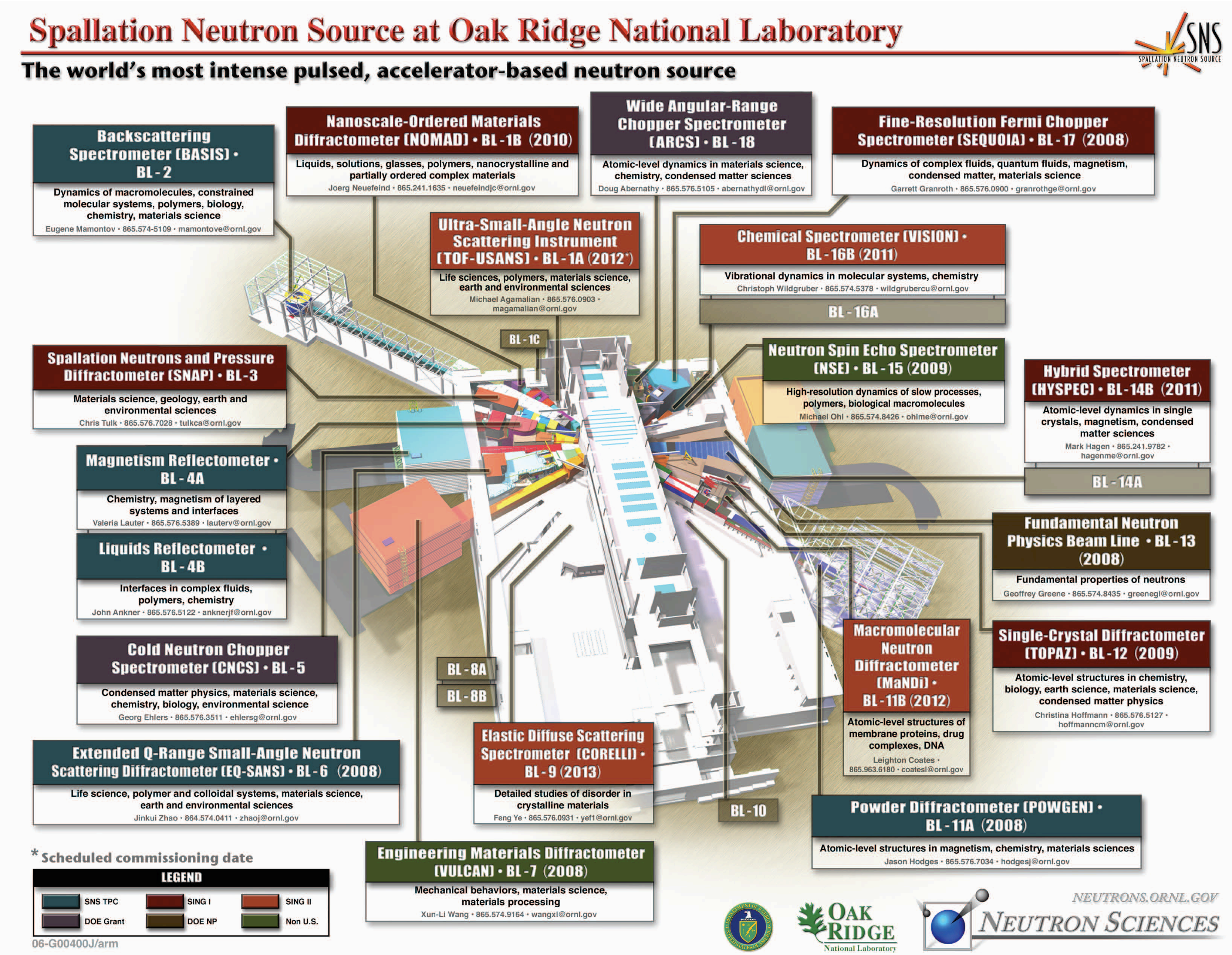


Fig. 3. Horizontal cross-section of the flux-trap moderators.





Spallation Neutron Source at Oak Ridge National Laboratory
The world's most intense pulsed, accelerator-based neutron source
SNS
SPALLATION NEUTRON SOURCE
Backscattering Spectrometer (BASIS) • BL-2
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Eugene Mamontov • 865.574-5109 • mamontove@ornl.gov
Nanoscale-Ordered Materials Diffractometer (NOMAD) • BL-1B (2010)
Liquids, solutions, glasses, polymers, nanocrystalline and partially ordered complex materials
Joerg Neuefeind • 865.241.1635 • neuefeindjc@ornl.gov
Wide Angular-Range Chopper Spectrometer (ARCS) • BL-18
Atomic-level dynamics in materials science, chemistry, condensed matter sciences
Doug Abernathy • 865.576.5105 • abernathydl@ornl.gov
Fine-Resolution Fermi Chopper Spectrometer (SEQUOIA) • BL-17 (2008)
Dynamics of complex fluids, quantum fluids, magnetism, condensed matter, materials science
Garrett Granroth • 865.576.0900 • granrothge@ornl.gov
Ultra-Small-Angle Neutron Scattering Instrument (TOF-USANS) • BL-1A (2012*)
Life sciences, polymers, materials science, earth and environmental sciences
Michael Agamalian • 865.576.0903 • magamalian@ornl.gov
Chemical Spectrometer (VISION) • BL-16B (2011)
Vibrational dynamics in molecular systems, chemistry
Christoph Wildgruber • 865.574.5378 • wildgrubercu@ornl.gov
BL-16A
BL-1C
Spallation Neutrons and Pressure Diffractometer (SNAP) • BL-3
Materials science, geology, earth and environmental sciences
Chris Tulk • 865.576.7028 • tulkca@ornl.gov
Neutron Spin Echo Spectrometer (NSE) • BL-15 (2009)
High-resolution dynamics of slow processes, polymers, biological macromolecules
Michael Ohl • 865.574.8426 • ohlme@ornl.gov
Hybrid Spectrometer (HYSPEC) • BL-14B (2011)
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Mark Hagen • 865.241.9782 • hagenme@ornl.gov
BL-14A
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Chemistry, magnetism of layered systems and interfaces
Valeria Lauter • 865.576.5389 • lauterv@ornl.gov
Liquids Reflectometer • BL-4B
Interfaces in complex fluids, polymers, chemistry
John Ankner • 865.576.5122 • anknerjf@ornl.gov
Fundamental Neutron Physics Beam Line • BL-13 (2008)
Fundamental properties of neutrons
Geoffrey Greene • 865.574.8435 • greenegl@ornl.gov
Cold Neutron Chopper Spectrometer (CNCS) • BL-5
Condensed matter physics, materials science, chemistry, biology, environmental science
Georg Ehlers • 865.576.3511 • ehlersg@ornl.gov
BL-8A
BL-8B
Macromolecular Neutron Diffractometer (MaNDi) • BL-11B (2012)
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Leighton Coates • 865.963.6180 • coatesl@ornl.gov
Single-Crystal Diffractometer (TOPAZ) • BL-12 (2009)
Atomic-level structures in chemistry, biology, earth science, materials science, condensed matter physics
Christina Hoffmann • 865.576.5127 • hoffmanncm@ornl.gov
Extended Q-Range Small-Angle Neutron Scattering Diffractometer (EQ-SANS) • BL-6 (2008)
Life science, polymer and colloidal systems, materials science, earth and environmental sciences
Jinkui Zhao • 864.574.0411 • zhaoj@ornl.gov
Elastic Diffuse Scattering Spectrometer (CORELLI) • BL-9 (2013)
Detailed studies of disorder in crystalline materials
Feng Ye • 865.576.0931 • yef1@ornl.gov
BL-10
Powder Diffractometer (POWGEN) • BL-11A (2008)
Atomic-level structures in magnetism, chemistry, materials sciences
Jason Hodges • 865.576.7034 • hodgesj@ornl.gov
* Scheduled commissioning date
LEGEND
SNS TPC
SING I
SING II
DOE Grant
DOE NP
Non U.S.
Engineering Materials Diffractometer (VULCAN) • BL-7 (2008)
Mechanical behaviors, materials science, materials processing
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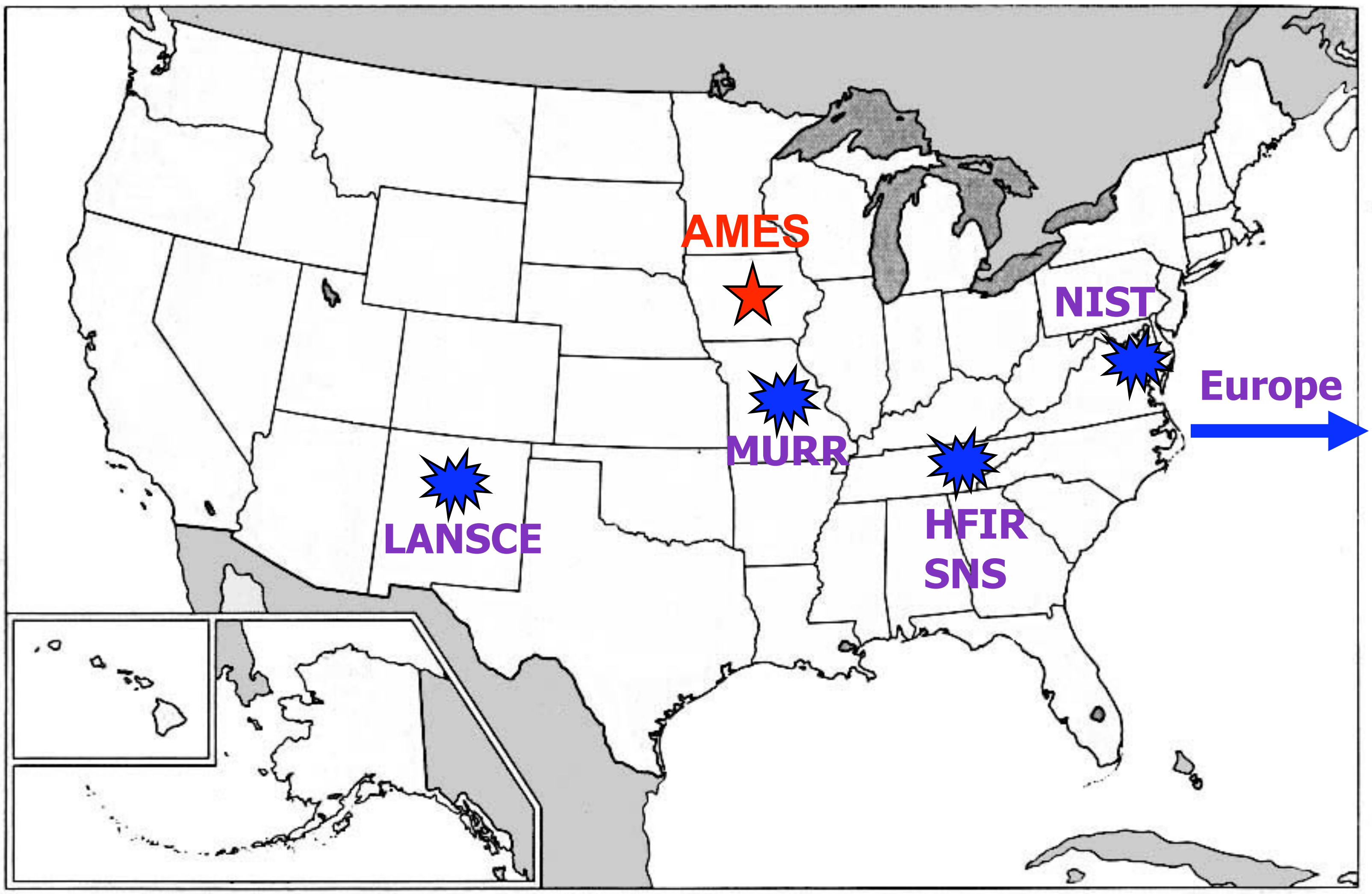
RY

Places to go

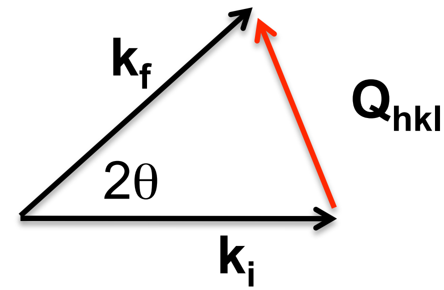


Powder diffraction

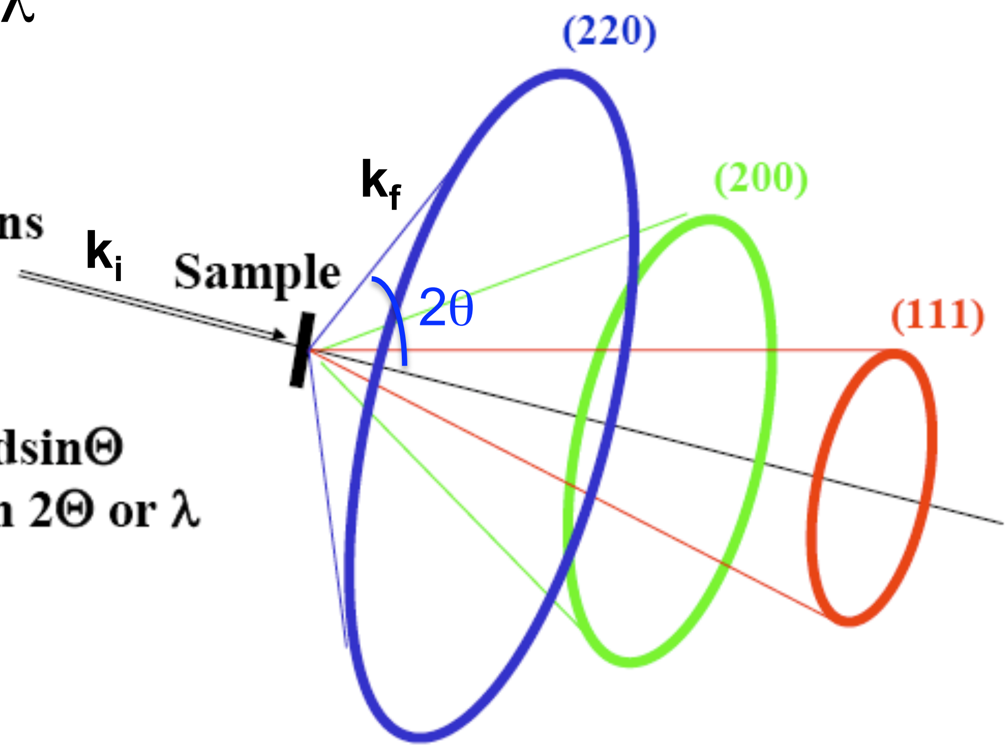
For single-crystal: $\mathbf{Q_{hkl}} = \mathbf{k_f} - \mathbf{k_i}$

For powder: $Q_{hkl} = 2k_i\sin\theta$

$k_i = 2\pi/\lambda$



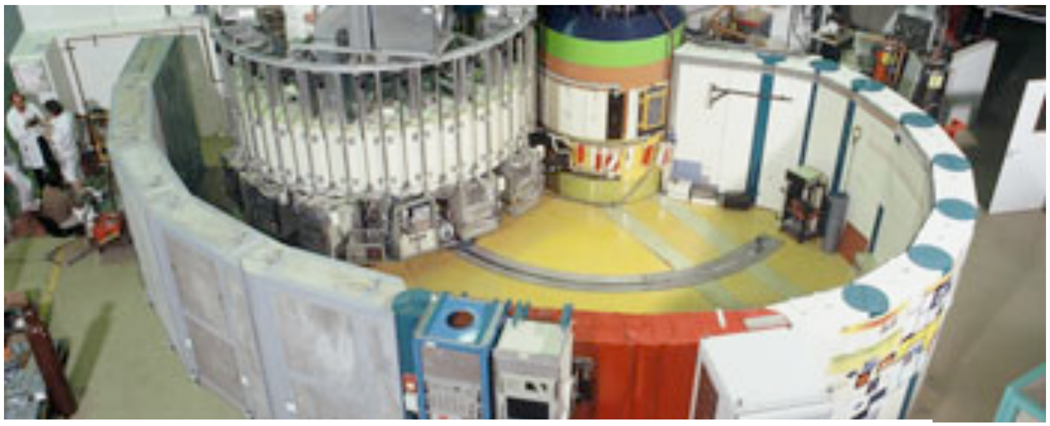
Incident beam
x-rays or neutrons

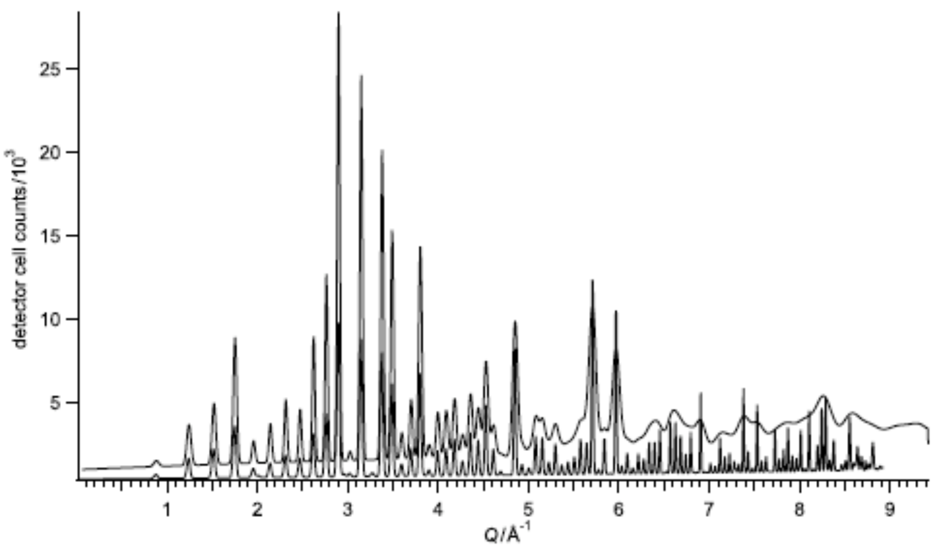


Bragg's Law $\lambda = 2d\sin\Theta$
Powder pattern – scan 2Θ or λ

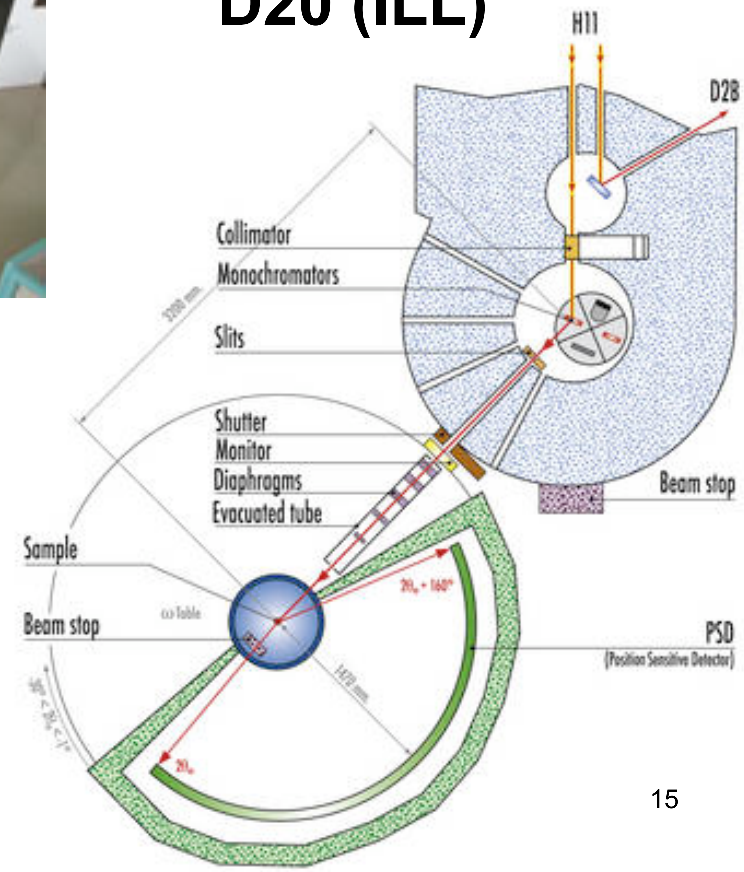
Powder diffraction

Determine the crystal structure





D20 (ILL)



TOF powder diffraction

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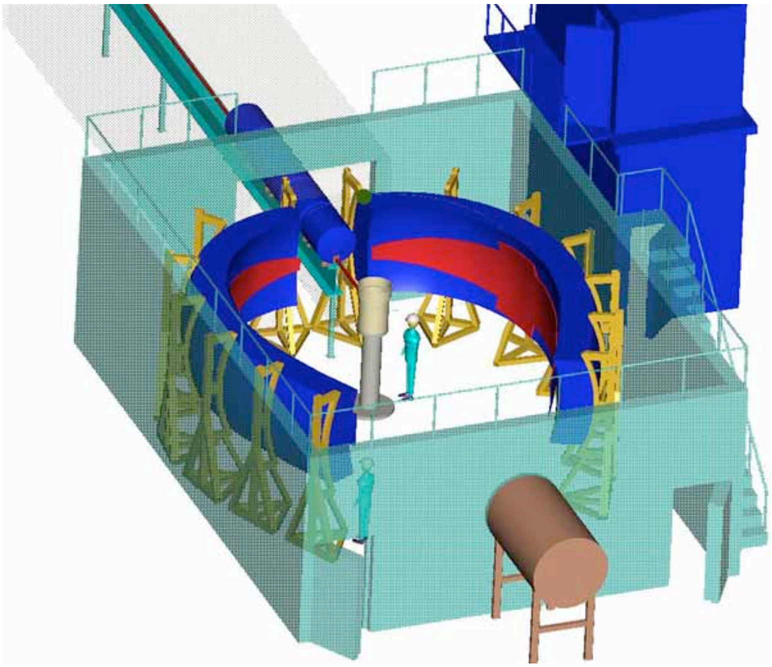
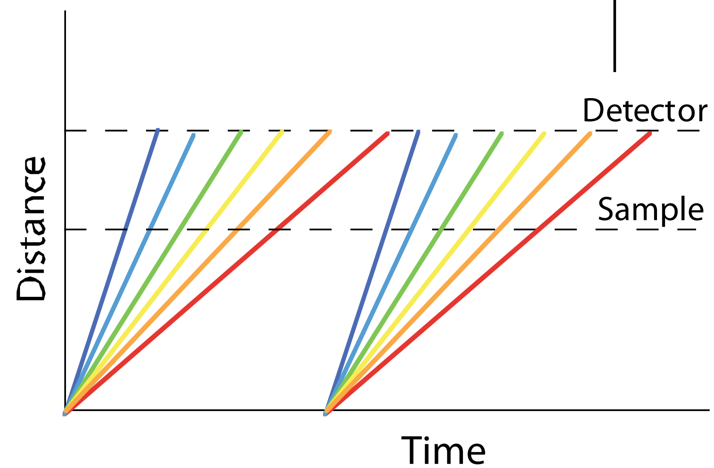
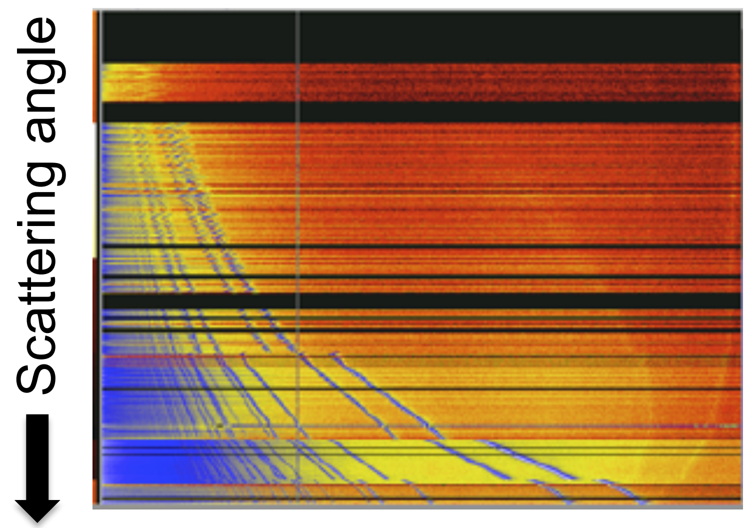


POWGEN @ SNS

Time-of-flight
$\tau = L/v = \lambda mL/h = 2mLd\sin\theta/h$





Fitting diffraction data

- **Rietveld refinement**
  - Lattice constants
  - space group
  - Atom positions
  - Site disorder/vacancies
  - Thermal vibration amplitude
  - Strain broadening
  - R-factor

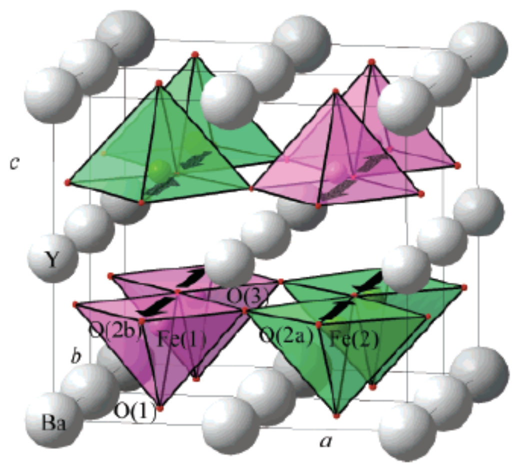


Figure 3. Crystal and magnetic structure of the class-I MV (charge-ordered) $YBaFe_2O_5$ at 20 K. Magnetic unit cell ($a \times 2b \times c$) is drawn.

Table 4. $YBaFe_2O_5$ Structure Refinement Results from NPD Data

T (K):	20	280	300	320	340
λ (Å)	1.5402	2.0783	2.0783	2.0783	2.0783
R_{wp}	0.0671	0.0789	0.0907	0.0783	0.0748
χ^2	4.78	1.38	1.91	1.25	1.17
space group	$Pmma^a$	$Pmma^a$	$Pmma^a$	$Pmmm^b$	$Pmmm^b$
a (Å)	8.0251(1)	8.0162(2)	8.0141(2)	3.93329(7)	3.93181(7)
b (Å)	3.83834(6)	3.85238(7)	3.85511(9)	3.91342(7)	3.91717(7)
c (Å)	7.5312(1)	7.5541(2)	7.5577(2)	7.5652(1)	7.5683(1)
$a_s - b_s$(Å)^c	0.1742	0.1557	0.1520	0.0199	0.0146
V (Å^3)	231.983(8)	233.28(1)	233.49(1)	116.447(5)	116.563(5)
Fe(1) z	0.2542(4)	0.2568(9)	0.257(1)	0.2640(2)	0.2641(2)
Fe(2) z	0.2695(4)	0.2662(9)	0.265(1)		
O(1) z	0.003(1)	0.001(3)	0.000(3)	0	0
O(2a) z	0.3213(7)	0.324(2)	0.325(2)	0.3137(5)	0.3140(6)
O(2b) z	0.3132(7)	0.307(2)	0.308(2)		
O(3) x	0.0098(7)	0.012(1)	0.011(2)	0	0
O(3) z	0.3119(3)	0.3130(4)	0.3115(4)	0.3127(5)	0.3125(6)
Y U_{iso} (Å^2)	0.0063(4)	0.0123(9)	0.013(1)	0.0152(8)	0.0137(7)
Ba U_{iso} (Å^2)	0.0039(6)	0.014(1)	0.017(1)	0.017(1)	0.0144(9)
Fe U_{iso}/U_{eqv} (Å^2)^{d,e}	0.0039(3)	0.0124(6)	0.0139(8)	0.0132	0.0122
O(1) U_{eqv} (Å^2)^d	0.0080	0.0138	0.0159	0.0181	0.0136
O(2) U_{eqv} (Å^2)^{d,f}	0.0065	0.0123	0.0129	0.0186	0.0188
O(3) U_{eqv} (Å^2)^d	0.0078	0.0128	0.0141	0.0146	0.0138
Fe M_y (μ_B)	3.82(2)	3.41(3)	3.26(3)	2.88(2)	2.76(2)
Fe M_z (μ_B)	0	0	0	−0.17(8)	−0.20(8)
Fe M_{Total} (μ_B)	3.82(2)	3.41(3)	3.26(3)	2.89(2)	2.77(2)

[a] Wyckoff positions for space group *Pmma* (nuclear cell) are: Ba at 2a (0,0,0); Y at 2c (0,0,$^1/_2$); Fe(1) and O(1) at 2f ($^1/_4$,$^1/_2$,z); Fe(2) at 2f ($^3/_4$,$^1/_2$,z); O(2a) at 2e ($^3/_4$,0,z); O(2b) at 2e ($^1/_4$,0,z); O(3) at 4j (x,$^1/_2$,z). [b] Wyckoff positions for space group *Pmmm* (nuclear cell) are: Ba at 1a (0,0,0); Y at 1c (0,0,$^1/_2$); Fe at 2t ($^1/_2$,$^1/_2$,z); O(1) at 1f ($^1/_2$,$^1/_2$,0); O(2) at 2s ($^1/_2$,0,z); O(3) at 2r (0,$^1/_2$,z). [c] Orthorhombic distortion; refers to the single-perovskite-type subcell. [d] U_{eqv} values are given for those atoms where anisotropic displacement parameters were used in the refinement. The U_{eqv} values are defined as one-third the trace of the diagonal matrix describing the shape of the thermal ellipsoid. A complete list of the anisotropic displacement parameters is given in the Supporting Information. [e] The displacement parameters for Fe(1) and Fe(2) were constrained to be equal. An isotropic displacement parameter was used in the charge-ordered state; anisotropic displacement parameters were used for the MV state. [f] The displacement parameters for O(2a) and O(2b) were constrained to be equal.

Caution !!!

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Things to keep in mind about powder diffraction measurements

• Easy to do, but make sure you have a good powder!!!

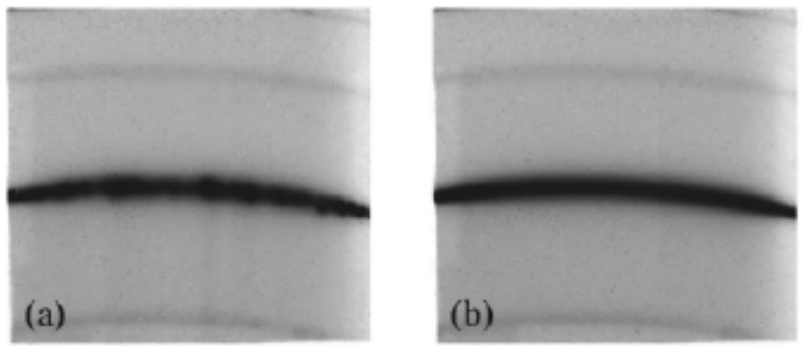


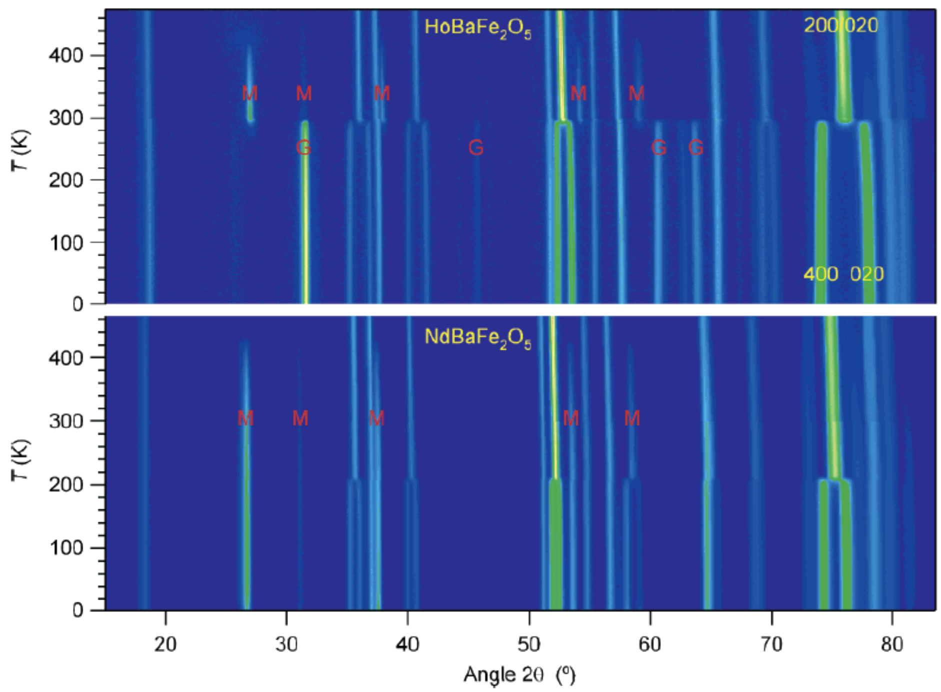
FIG. 9. CCD image of Fe_3Al powder (a) taken with stationary sample and (b) taken with sample rotation.

• Powder diffraction is excellent for getting the "big picture" but since intensities are spread over a sphere, small (but perhaps important) details are missed.

• Lose information about anisotropy

Thermodiffractometry

Detailed parameter dependence



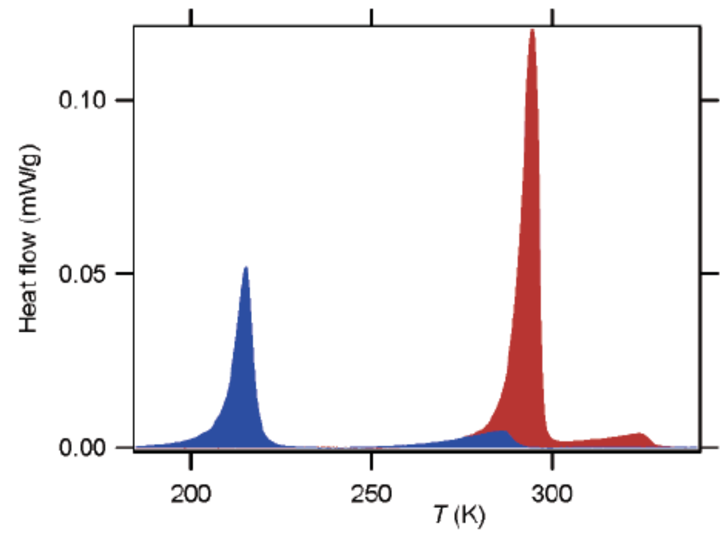
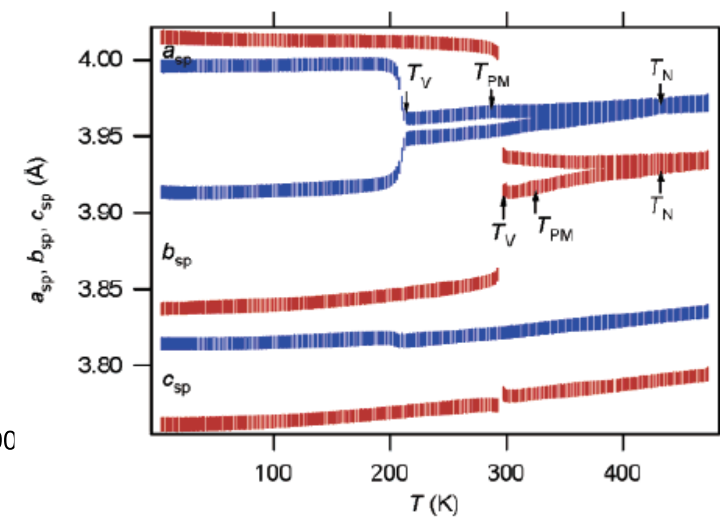


Figure 2. DSC peaks for NdBaFe$_2$O$_5$ (blue) and HoBaFe$_2$O$_5$ (red) upon heating. Areas give latent heat (ΔH) of the charge-ice melting.



High-flux mode leads to high data rates

Single-crystal diffraction

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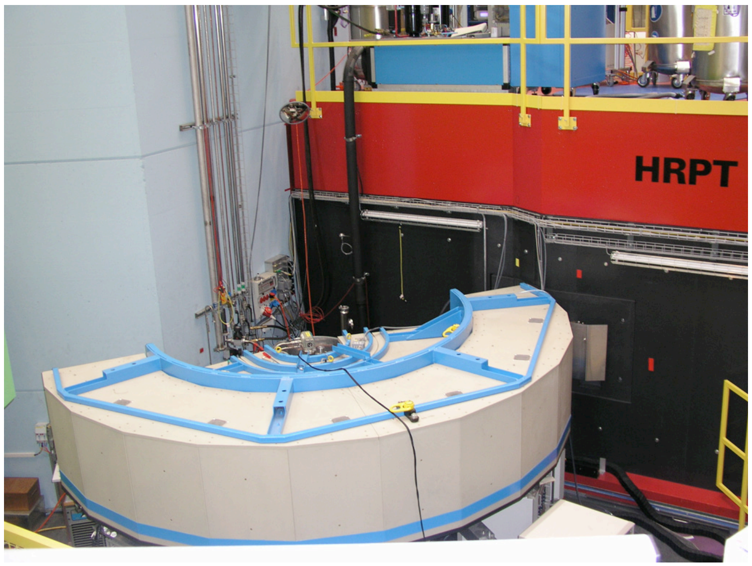
Single-crystal: more detail than powders
Wide angle diffraction: Get an overview of everything



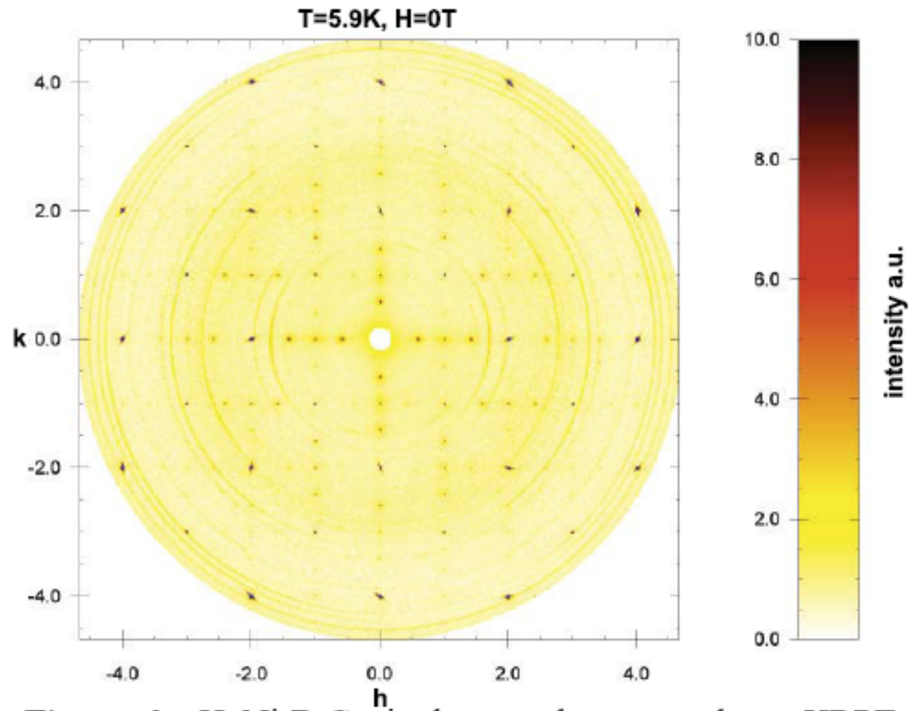
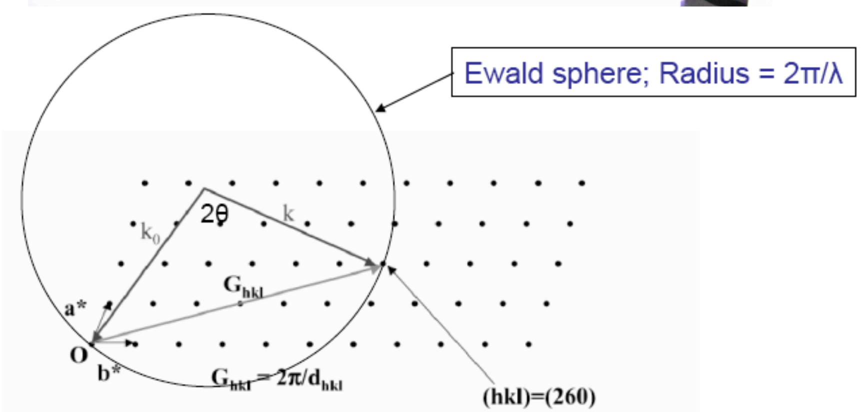
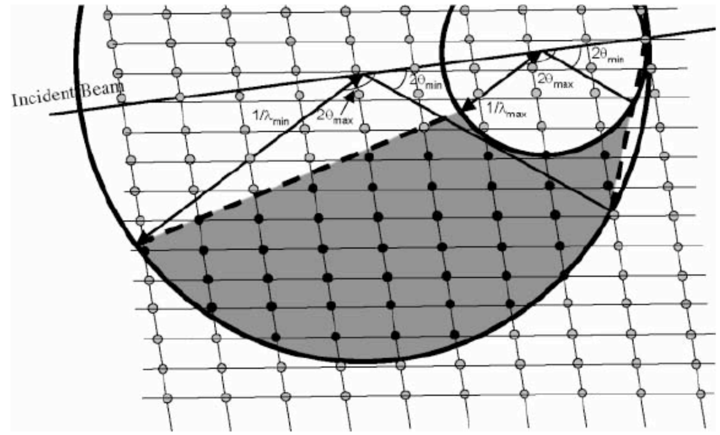


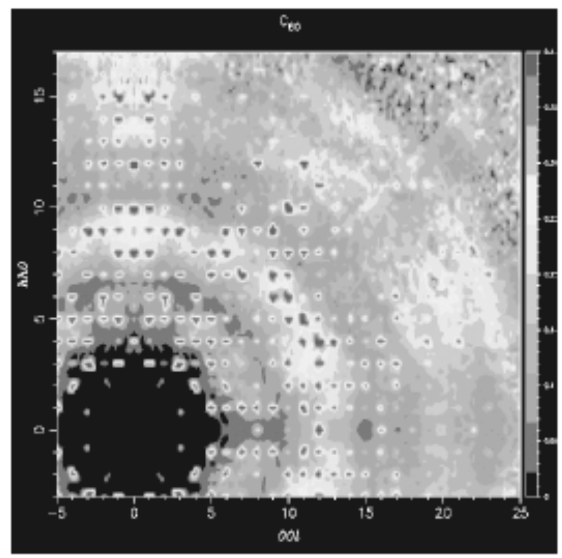
Figure 2: $HoNi_2B_2C$ single-crystal measured on HRPT



Incommensurate magnetism

TOF single-xtal diffraction

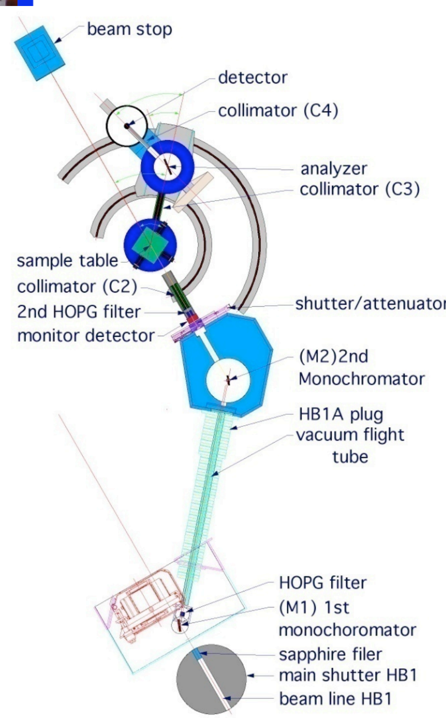


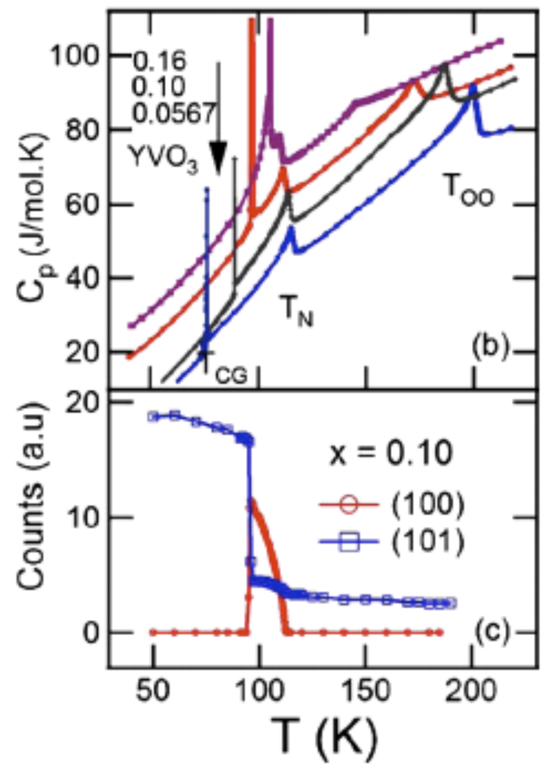


Single crystal diffraction

Triple-axis diffraction: focus in on specific points of interest

HB-1A 3-axis spectrometer





Orbital ordering in YVO_3

Further references

- **General neutron scattering**
  - G. Squires, “Intro to theory of thermal neutron scattering”, Dover, 1978.
  - S. Lovesey, “Theory of neutron scattering from condensed matter”, Oxford, 1984.
  - R. Pynn, http://www.mrl.ucsb.edu/~pynn/.
- **Structural refinements**
  - GSAS http://www.ncnr.nist.gov/xtal/software/gsas.html
  - FullProf
    http://www.ill.eu/sites/fullprof/
- **How to get beam time**
  - Talk to one of us at Ames about your experiment
  - We can identify a suitable instrument
  - Talk to instrument scientist
  - Write a beamtime request